

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 336 668 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
20.08.2003 Bulletin 2003/34

(51) Int Cl.7: **C23C 16/455, C23C 16/40**

(21) Application number: **03250497.9**

(22) Date of filing: **28.01.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT SE SI SK TR**
Designated Extension States:
AL LT LV MK RO

• **Fukazawa, Atsuki**
Tama-shi, Tokyo 206-0025 (JP)
• **Morisada, Yoshinori**
Tama-shi, Tokyo 206-0025 (JP)
• **Kato, Manabu**
Tama-shi, Tokyo 206-0025 (JP)

(30) Priority: **29.01.2002 US 352718 P**

(71) Applicant: **ASM JAPAN K.K.**
Tama-shi, Tokyo 206-0025 (JP)

(74) Representative: **Mallalieu, Catherine Louise et al**
D. Young & Co.,
21 New Fetter Lane
London EC4A 1DA (GB)

(72) Inventors:
• **Matsuki, Nobuo**
Tama-shi, Tokyo 206-0025 (JP)

(54) **Method for forming insulation film**

(57) An insulation film is formed on a semiconductor substrate by a method including the steps of: (i) introducing a source gas comprising a compound composed of at least Si, C, and H into a chamber; (ii) introducing

in pulses an oxidizing gas into the chamber, wherein the source gas and the oxidizing gas form a reaction gas; and (iii) forming an insulation film on a semiconductor substrate by plasma treatment of the reaction gas. The plasma treatment may be plasma CVD processing.

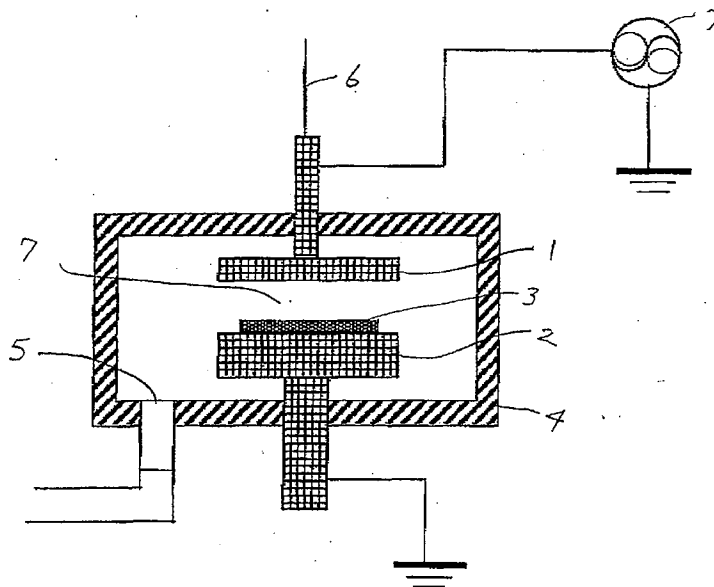


Fig. 1

EP 1 336 668 A1

DescriptionBackground of the Invention5 Description of the Related Art

[0001] Because of the recent rise in requirements for the large-scale integration of semiconductor devices, a multi-layered wiring technique attracts a great deal of attention. These multi-layered structures, however, capacitance among individual wires hinders high-speed operations. In order to reduce the capacitance it is necessary to reduce the dielectric constant (relative permittivity) of the insulation film. Thus, various materials having a relatively low dielectric constant have been developed for insulation films.

[0002] As shown in the table below, along with reduction of a device node, a low dielectric constant value (Low-k) is required for an interlayer insulation film used for the device concerned.

15

Time to be applied	Device Node	k Value
2001	130nm	3.0-3.6
2003	100nm	3.0-3.6
2005	80nm	2.6-3.1
2007	65nm	2.3-2.7

20

[0003] As to Low-k films with a dielectric constant of approximately 2.7, because many deposition methods such as a CVD method, coating method, etc. have been proposed, high-quality Low-k deposition becomes possible in recent years. As a result, application of the films to mass-produced devices with a device node of 0.10 to 0.13 μ m has just started. For next-generation high-speed devices, Low-k films having a furthermore lower dielectric constant of approximately $k=2.5$ or less will be required. Additionally, to manufacture devices, improving reliability of the devices is attempted by incorporating a hard layer being relatively hard with a high dielectric constant on the top, intermediate or the bottom surface of the Low-k film. Because a dielectric constant increases if the hard layer is incorporated in this way, Low-k films with a low dielectric constant as much as possible are required.

30

Summary of the Invention

[0004] The present invention enables forming a low dielectric constant film of $k<2.40$ by introducing a pulse control flow of oxidizing gas into a gas containing silicon gas using a CVD method. Further, although conventional methods for controlling oxygen are different from the present invention, the present invention can be applied to conventional apparatus and make it possible to reduce capital investment manufacturing costs because CVD Low-k deposition devices for approximately $k=2.7$ deposition can easily be modified and used for the present invention. In the present invention, oxidizing gas is introduced in pulses and is mixed with and made to react with a source gas (material gas for forming a film) comprising silicon in a reaction zone. By pulse-controlling the flow of oxidizing gas in plasma CVD processing, the reactivity of the reaction gas (composed of the source gas and the oxidizing gas) can effectively be controlled, forming a low dielectric constant film. The residence time of the reaction gas in the reaction zone or the type of silicon-containing gas such as $\text{Si}_\alpha\text{O}_{\alpha-1}\text{R}_{2\alpha-\beta+1}(\text{OCH}_n\text{H}_{2n+1})_\beta$ gas is not prerequisites for practicing the present invention. However, these factors may be controlled, and in embodiments, DM-DMOS (Dimethyldimethoxysilane, $\text{Si}(\text{CH}_3)_2(\text{OCH}_3)_2$) and oxygen may be used, oxygen may be used as an oxidizing agent, and a low-dielectric film may be formed, as disclosed in United States patent application No. 09/827,616, filed April 6, 2002. The disclosure of the application is herein incorporated by reference in its entirety.

45

[0005] In an embodiment, the present invention provides a method for forming an insulation film on a semiconductor substrate, comprising the steps of: (i) introducing a source gas comprising a compound composed of at least Si, C, and H into a chamber; (ii) introducing in pulses an oxidizing gas into the chamber, wherein the source gas and the oxidizing gas form a reaction gas; and (iii) forming an insulation film on a semiconductor substrate by plasma treatment of the reaction gas. In the above, the plasma treatment may be plasma CVD processing. The plasma CVD processing includes plasma-enhanced CVD (PECVD) processing and remote plasma processing in which the reaction zone and the film formation zone are different. Any suitable CVD processing can be employed.

50

[0006] Increasing a flow of oxidizing gas increases the reactivity of the reaction zone and the size of fragments formed in the reaction zone, which lowers the dielectric constant value because a film obtained includes vacancies or pores between fragments accumulated. It is inferred that when an oxidizing gas flow increases, the size of fragments forming in the reaction zone increases, a vacancy rate or porosity of the film increases and a dielectric constant de-

55

creases. However, lowering a k value up to approximately 2.45 appears to be the limit even if the flow of oxidizing gas increases. If the oxygen amount increases more, dust is generated in the reaction zone and high-quality films cannot be obtained, and these films may not possess any measurable dielectric constant. Additionally, plasma becomes unstable and a stable reaction cannot be maintained. In the present invention, by introducing an oxidizing gas in pulses, surprisingly, the above problems can be eliminated.

[0007] In an embodiment, the compound is an organo silicon of SixCyOzHa wherein a, x, y, and z are integers. The source gas comprises silicon-containing gas and optionally inert gas such as H and Ar (e.g., less than a half of the silicon-containing gas). The oxidizing gas may be included in an additive gas which may further include inert gas or reducing gas, depending on the reaction of film formation.

[0008] The oxidizing gas may be introduced in the chamber in cycles of 5msec to 10sec, although the duration of one cycle can be shorter or longer than the above, including 1msec and 20sec, depending on the reaction of film formation. A pulse cycle is repeated multiple times, e.g., 2-10,000 times including 10, 100, 1,000 times, during the film formation process. In an embodiment, the oxidizing gas is introduced in the chamber in cycles of 100msec to 5sec. The oxidizing gas can be oxygen, N_2O , or any other gas which can function as an oxidizing agent, including CO_2 , H_2O ; a cyclic organic compound having the formula $(\text{CH}_2\text{O})_n$ such as 1,3,5-trioxan; or an alkanol compound having the formula $\text{C}_x\text{H}_{2x+1}\text{OH}$ (x is an integer) such as ethanol, methanol, n-propanol, or i-propanol. In the above, alkanol itself is considered to be a reducing agent, but when alkanol is mixed with an organo silicon gas for film formation, a source gas oxidation reaction occurs. Thus, alkanol functions as an oxidizing agent. The usable oxidizing agent is not limited to the above and any of the foregoing can be used singly or in any combination.

[0009] In an embodiment, the introduction of the oxidizing gas in pulses can be achieved by introducing alternately (i) a first reaction gas comprising the source gas at a base flow rate and the oxidizing gas at a flow rate of 50% or higher of the base flow rate, and (ii) a second reaction gas comprising the source gas at a base flow rate and no oxidizing gas or the oxidizing gas at a flow rate of 50% or less of the base flow rate. The total flow of the oxidizing gas may be less than the flow of the source gas or in an embodiment, less than 50% of the source gas.

[0010] In the present invention, the pulses and the flow of the oxidizing gas can be selected so as to adjust a dielectric constant of the insulation film to 2.45 or less.

[0011] A plasma may be formed by RF power, although microwave power can be used in an embodiment. Further, when RF power is used, the intensity of RF power may be pulsed in cycles synchronized with the pulsed flow of the oxidizing gas, so that low-dielectric films can effectively be formed. In an embodiment, the intensity of RF power is higher in cycles when the oxidizing gas flow is low than in cycles when the oxidizing gas flow is high. In an embodiment, the intensity of RF power may be pulsed in cycles of 1msec or more, independently of the pulses of the oxidizing gas flow.

[0012] Additionally, the formation of the insulation film may be conducted while maintaining a temperature of a shower plate at 150°C or higher, through which the reaction gas passes into the chamber.

[0013] The insulation film may be a cap layer having a thickness of 10nm or more in an embodiment, although the type or usage of film should not be limited.

[0014] The present invention enables forming of a low dielectric constant film in the plasma CVD method. By using this low dielectric constant film as an insulation film for next-generation highly integrated semiconductor elements, delay caused by wiring capacity can be lowered and the operation speed of a semiconductor element can be substantially increased.

[0015] For purposes of summarizing the invention and the advantages achieved over the prior art, certain aims and advantages of the invention have been described above. Of course, it is to be understood that not necessarily all such aims or advantages may be achieved in accordance with any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other aims or advantages as may be taught or suggested herein.

[0016] Further aspects, features and advantages of this invention will become apparent from the detailed description of the preferred embodiments which follow.

Brief Description of the Drawings

[0017]

Figure 1 is a schematic diagram illustrating a plasma CVD apparatus used for forming an insulation film.

Figure 2 is a graph showing the relationship between k values of insulation films and non-pulsed oxidizing gas flow.

Detailed Description of the Preferred Embodiment

[0018] An embodiment, the present invention is characterized in that oxidizing gas is introduced in a pulse cycle.

[0019] This feature is applicable to and effective in any methods for forming a low-k film using an oxidizing gas for a silicon gas.

[0020] Production processes to which the present invention is applied are not limited. For example, the present invention can be applied to a method for forming a low-k polysiloxian polymer film wherein the residence time of a reaction gas is controlled. One example of such a method is United States Patent Application Publication No. US 2001/0046567 A1, filed April 6, 2001. The disclosure of the U.S. patent application is herein incorporated by reference in its entirety.

[0021] In the present invention, the type of material gas usable is not limited to those disclosed in the above United States Patent Application, and it can be selected from a variety of material gases. For example, usable is an organic silicon gas such as $\text{Si}_x\text{O}_{x-1}\text{R}_{2x-y+1}(\text{OC}_n\text{H}_{2n+1})_y$, wherein x is an integer of 1-3, y is 0, 1, or 2, n is an integer of 1-3, and R is C1-6 hydrocarbon attached to Si, and $\text{Si}_x\text{O}_{x-1}\text{R}_{2x+1}$, wherein x is an integer of 1-3, and R is C1-6 hydrocarbon attached to Si.

[0022] Usable material gas may include $\text{Si}(\text{CH}_3)_3\text{-O-Si}(\text{CH}_3)_3$, $\text{Si}(\text{CH}_3)_3\text{-O-Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_3$.

[0023] Usable material gas may further include $\text{SiH}_n(\text{CH}_3)_{4-n}$, $\text{Si}(\text{CH}_3)_4$, $\text{Si}(\text{CH}_3)_3$, SiH_4 .

[0024] United States patent No. 6,455,445 issued September 24, 2002, No. 6,352,945 issued March 5, 2002, No. 6,383,955 issued May 7, 2002, No. 6,410,463 issued June 25, 2002, and No. 6,432,846 issued August 13, 2002, disclose material gases which are also usable in the present invention. The disclosure of each U.S. patent application is herein incorporated by reference in its entirety.

[0025] An aim of the present invention in one embodiment is forming a low-k film, and not only an organic silicon gas but also a silicon gas such as SiH_4 can be used, and by introducing an oxidizing gas in a pulse cycle, a film having a porous structure can effectively be formed.

[0026] Further, in the present invention, any suitable CVD apparatuses can be used including an apparatus wherein an intermediate electrode is disposed between an upper electrode and a lower electrode. For example, the present invention can be applied to apparatuses and methods disclosed in United States patent Application Publication No. US 2002/0168870 A1, filed May 9, 2001. The disclosure of the U.S. patent application is herein incorporated by reference in its entirety.

[0027] By introducing an oxidizing gas in a pulse cycle, the sum of introduced oxidizing gas can be increased. That is, if the flow of oxidizing gas increases, dust (nano-particles) increases, causing a plasma to be unstable due to an increase in reactivity. By introducing an oxidizing gas in a pulse cycle, it is possible to increase the flow of oxidizing gas while suppressing the formation of dust (nano-particles) or stopping the growth of it at some size of the dust.

[0028] The cycled introduction of oxidizing gas is effective in stabilizing a plasma by suppressing growth of nano-particles, regardless of the amount of introduced oxidizing gas. Even when at a low flow of oxidizing gas, by introducing it in a pulse cycle, a low-k film can effectively and stably be formed as compared with constant introduction of oxidizing gas. In a low flow oxidizing gas step, reactivity decreases, while in a high flow oxidizing gas step, reactivity increases, suppressing growth of nano-particles (dust) and stabilizing a plasma. A high quality of a low-k film can be formed.

[0029] Oxidizing gas can be introduced in a pulse cycle which includes the following:

[0030] The oxidizing gas flow in high flow steps is higher than that in low flow steps to any degree.

[0031] For example, in oxidizing gas high flow steps, the oxidizing gas flow may be approximately 50% or higher of the silicon gas flow, preferably 50% to 300% (including 100% to 200%). In an embodiment, this may be approximately 50sccm to 500sccm of oxidizing gas (including 100sccm to 300sccm).

[0032] In oxidizing gas low flow steps, the oxidizing gas flow may be approximately 50% or lower of the silicon gas flow, preferably 0% to 50% (including 10% to 30%). In an embodiment, this may be approximately 0sccm to 100sccm of oxidizing gas (including 10sccm to 50sccm).

[0033] One cycle of the high flow and the low flow is set at approximately 10msec to 10sec, preferably 0.05sec to 5sec (including 0.1sec to 1sec).

[0034] The cycles may be in an on-off pulse (e.g., a digital pulse) or in a sin wave (e.g., an analogue pulse), or in any other waves.

[0035] The cycled introduction of oxidizing gas can be conducted at all times when oxidizing gas is introduced or only after the flow of oxidizing gas exceeds a certain level where the introduction of oxidizing gas may cause a plasma to be unstable (e.g., at more than 50% of silicon gas).

[0036] Oxidizing gas may be O_2 , N_2O , or any other gas which is capable of causing oxidization during polymerization by plasma reactions.

[0037] A reaction gas may include a silicon gas and an oxidizing gas, and if suitable, an inert gas such as He, Ar, and Kr. These gas flows may be controlled separately by gas controllers.

[0038] The plasma reaction's conditions and apparatuses can be those disclosed in any of the above mentioned U.

S. patent applications.

Example

- 5 **[0039]** An embodiment of the present invention will be explained with reference to figures and examples. However, the present invention should not be limited to this embodiment.

Device Configuration

- 10 **[0040]** Figure 1 is a view showing a parallel-flat-plate type of a CVD device using a capacity-coupling system usable in the present invention. By placing two pairs of conductive flat-plate electrodes 1, 2 in parallel and facing each other in a reaction chamber 4, and by applying 27MHz RF power 7 to one side and grounding the other side, a plasma is excited between these two pairs of electrodes 1, 2. A substrate 3 is placed on the lower electrode 2. A temperature regulator is installed in the lower stage 2 and a constant temperature of approximately 400°C (400°C to 450°C in other
15 embodiments) is kept in the lower stage. DM-DMOS (Dimethyldimethoxysilane, $\text{Si}(\text{CH}_3)_2(\text{OCH}_3)_2$), inactive gas such as He, Ar and Kr and oxidizing gas such as O_2 and N_2O are mixed and used as a reaction gas. A flow of these gases is regulated respectively at a prescribed flow by flow regulators (now shown). These gases are mixed and are introduced into an inlet port 6 provided at the top of an upper electrode (shower plate) 1 as a reaction gas. Regarding a flow of oxidizing gas, two steps, a prescribed relatively large flow (approximately 50sccm to 500sccm) that is half to approx-
20 imately 3 times larger than a flow of silicon gas and a prescribed relatively smaller flow (approximately 0sccm to 100sccm) that is zero to approximately half to a flow of silicon gas, are repeated by pulse control in cycles of approximately 10msec to 10 sec. In the upper electrode 1, 500 to 10,000 fine pores with a diameter of approximately 0.5mm are made (3,000 fine pores were made in the embodiment), and the reaction gas introduced flows into the reaction zone 7 through these fine pores. Additionally, the upper electrode 1 is kept at a constant temperature in a range of
25 120°C to 350°C. To promote reaction of the reaction gas, a higher temperature is preferable. The air in the reaction zone 7 is exhausted using a vacuum pump through an exhaust port 5 and a pressure in the reaction zone is kept at a prescribed constant pressure of approximately 130 Pa to 2,000 Pa (400 Pa to 1,000 Pa in other embodiments).

Deposition reaction

- 30 **[0041]** By adding DM-DMOS as material gas and O_2 to the reaction gas, a film of approximately $k=2.45$ was formed as described in U.S. Patent Application Publication No. US 2001/0046567 A1, filed April 6, 2001.
- [0042]** For comparison, a dielectric constant value of a film formed was measured by changing an amount of oxygen added to DM-DMOS using the plasma CVD device in which RF power was kept at a constant level by the technique
35 according to the present invention. With a pressure of 620 Pa, a temperature of the upper electrode (shower plate) kept at 240°C, and a susceptor temperature kept at 400°C, a film was formed with a gap between these electrodes, the shower plate and the susceptor, set to 24mm. In the reaction zone, 140 sccm of DM-DMOS and 80sccm of He were mixed. By changing a flow of oxygen added to the mixed gas from 0sccm to 70sccm, a dielectric constant value of a film formed under respective conditions was measured. At this time, 1000W of 27MHz RF power was applied. A
40 k value was 2.75 when O_2 added was 0sccm. The dielectric constant decreased by increasing a flow of oxygen added. By increasing O_2 to 70sccm, the dielectric constant decreased to $k=2.46$ (Figure 2).
- [0043]** However, if a flow of oxygen was increased above 70sccm, high-quality films could not be obtained because dust was generated in the reaction zone and was accumulated on the film as well. Additionally, particles generated disrupted a stable plasma position; hence deposition could not be carried on. For this reason, it was impossible to
45 increase a flow of oxygen further and it was impossible to lower the dielectric constant to below 2.45.
- [0044]** It is considered that increasing a flow of oxygen increases the reactivity of the reaction zone and the size of fragments formed in the reaction zone, which lowers the dielectric constant value because the film obtained includes vacancies or pores between fragments accumulated. It is inferred that when an oxygen flow increased, the size of fragments forming in the reaction zone increased, a vacancy rate or porosity of the film increased and a dielectric
50 constant decreased. However, lowering a k value up to approximately 2.45 is the limit in this method. If increasing an oxygen amount more than that, dust is generated in the reaction zone and high-quality films cannot be obtained, and the dielectric constant of these films cannot be measured. Additionally, a plasma becomes unstable and a stable reaction cannot be maintained.
- [0045]** The present invention can form a low dielectric constant film by pulsing oxygen to be introduced. Using the
55 same conditions as those of a comparative experiment (Pressure: 620Pa, RF Power (27MHz): 1000W, and DM-DMOS: 140sccm, He: 30sccm), oxygen was introduced by pulse control repeating steps of feeding 200sccm of oxygen for 0.5 sec and then 20sccm of oxygen for 0.5 sec. With this control, an average flow of 110sccm of oxygen was constantly flowing. In the case of a technique of a comparative example, when letting oxygen in an amount of 75sccm or more

flow, a plasma becomes unstable and stable deposition cannot be maintained. By introducing oxygen with pulse control, even when an average flow of 110sccm of oxygen was introduced, stable deposition was maintained and a low dielectric constant film with $k=2.35$ was obtained.

5 Experiment Results

<Common Conditions>

[0046]

- Reactor setting

Upper electrode (shower plate) temperature	240°C
Susceptor temperature	400°C
Gap between the shower plate and the susceptor	24mm

- Process conditions

DM-DMOS	140sccm
He	30sccm
RF Power 27 MHz	1000W
Pressure	620 Pa
Process Time for Film Formation	See the table below.

<Conditions for the comparative experiment>

[0047] Oxygen was introduced a steady state, deposition was performed on a Si substrate and a dielectric constant value was measured.

Oxygen Flow Added	Dielectric Constant	Process Time
0 sccm	2.75	245 sec
20 sccm	2.62	60 sec
60 sccm	2.50	19 sec
70 sccm	2.46	17 sec
75 sccm or more	Deposition was impossible due to unstable plasma	-

<Pulsed O₂ Process>

[0048] By introducing oxygen by pulse control repeating steps of feeding 180sccm of oxygen for 0.5 sec. and then 20sccm of oxygen for 0.5 sec., a low dielectric constant film was formed on a Si substrate and a dielectric constant was measured. With this control, an average flow of 110sccm of oxygen was constantly flowing. By introducing oxygen with pulse control, plasma remained stable and a low dielectric constant film with $k=2.35$ was obtained.

[0049] Additionally, in the end, by stopping flowing oxygen, and forming a protective film of 50nm only using DM-DMOS and He, preventing moisture absorption from without is possible.

[0050] In the present invention, an oxidizing gas is introduced into a chamber in pulses, and also, the intensity of RF power can be pulsed in cycles synchronized with the pulsed flow of the oxidizing gas. The above aspect can be accomplished in various ways. For example, the film formation process can be comprised of multiple steps of film formation which are continuously conducted in sequence. In different steps, the flow of an oxidizing gas and/or the intensity of RF power can be pulsed in different cycles. In another embodiment, the flow of an oxidizing gas and/or the intensity of RF power in pulses can be changed in different steps. Further, different steps can be comprised of at least one pulse-conducting step and at least one non-pulse-conducting step. For example, the process comprises two steps, wherein a first step is a pulse-conducting step, and a second step is a non-pulse-conducting step.

[0051] Further, in the present invention, a chamber into which an oxidizing gas is introduced in pulses need not be

a reaction chamber itself. The chamber can be any suitable reaction space which can be defined functionally and need not be defined by a physical structure. For example, if the reaction chamber is divided into several zones depending on the temperatures, pressures, and/or gas flows, a zone wherein plasma reaction takes place may be a reaction space.

[0052] The present invention can be realized in various embodiments which include but are not limited to the following:

- 1) By pulse control in a cycle of 1msec. or more, oxidizing gas is introduced in a reaction zone and a low dielectric constant film of $k < 3.0$ is formed in a CVD method.
- 2) By introducing in pulses oxidizing gas together with a reaction gas containing at least Si, C and H chemical elements, a low dielectric constant film is formed in the CVD method.
- 3) The method for forming a low dielectric film using oxygen or N_2O as the oxidizing gas used in Item 2.
- 4) The method as described in Item 3, wherein a low dielectric constant film is formed by a plasma CVD method using capacity coupling system.
- 5) In a method as described in Item 4, a low dielectric constant film is formed using a reaction gas containing at least an organic silicon gas of $Si_xCyOzHa$ (wherein a, x, y, z are integers of at least one).
- 6) A method for forming a low dielectric constant film, which uses $Si_\alpha O_{\alpha-1} R_{2\alpha-\beta+1} (OC_n H_{2n+1})_\beta$ (wherein α is an integer of 1 to 3, β is 0, 1 or 2, n is an integer of 1 to 3, and R is C_{1-6} hydrocarbon attached to Si) as the organic silicon gas as described in item 5.
- 7) A method for forming a low dielectric constant film, which uses $Si_\alpha O_{\alpha-1} R_{2\alpha+1}$ (wherein α is an integer of 1 to 3, R is C_{1-6} hydrocarbon attached to Si) as the organo silicon gas as described in Item 5.
- 8) A method for forming a low dielectric constant film, which uses $Si_4O_4(CH_3)_8$ or $Si_4O_4(CH_3)_4H_4$ as the organo silicon gas as described in Item 5.
- 9) A method for forming a low dielectric constant film, which uses Dimethyldimethoxysilane or Dimethoxytetramethyldisiloxane as the organo silicon gas as described in item 6.
- 10) A method for forming a low dielectric constant film, which introduces oxygen to be introduced in cycles of 5msec to 10sec.
- 11) A method for forming a low dielectric constant film, which introduces oxygen to be introduced in cycles of 100msec to 5sec.
- 12) A method for forming a low dielectric constant film by flowing oxygen to be added periodically in a cycle comprising a high-flow step in which a flow of oxygen is half or more of a flow of organic silane gas to be brought in as a material gas, and a low-flow step in which a flow of oxygen is half or less (including zero) of a flow of the organic silane gas, and using these mixed gases as a reaction gas.
- 13) A method for forming a low dielectric constant film with a dielectric constant of $k < 2.45$.
- 14) A method for forming a low dielectric constant film, wherein RF power is controlled at a high state and a low state in the same cycle as that of changing a flow of oxidizing gas.
- 15) A method for forming a low dielectric constant film, wherein RF power is raised at the timing that the concentration of oxidizing gas in a reaction zone is increased and is lowered at the timing that the concentration of the oxidizing gas is decreased.
- 16) A method for forming a low dielectric constant film, wherein RF power applied to the reaction zone is controlled at a high power state and at a low power state in a cycle of 1 msec. or more.
- 17) A low dielectric constant film is formed by maintaining a temperature of a shower plate at $150^\circ C$ or more.
- 18) A method for forming a low dielectric constant film, wherein by forming a Cap layer of 10nm or more with a flow of oxidizing gas at a rate used in the low-flow step or a small flow including zero thereof at the end of film formation, the final protective film is formed.

[0053] Further, the thin film formed by the present invention can be subjected to additional treatment to accomplish desired film properties. For example, upon completion of film formation, a thin cap film layer, which has a relatively high density and dielectric constant and has a thickness of 50-100nm, can be formed on the film surface in order to prevent moisture absorption phenomena when being exposed to the outer environment after the film formation. In order to render the film surface hydrophilic, the surface can be treated by exposing the film surface to an oxidizing gas plasma. Further, by radiating the film surface with electron rays or UV light, or by exposing the film surface to a plasma, the strength of the film can be improved.

[0054] It will be understood by those of skill in the art that numerous and various modifications can be made without departing from the spirit of the present invention. Therefore, it should be clearly understood that the forms of the present invention are illustrative only and are not intended to limit the scope of the present invention.

Claims

1. A method for forming an insulation film on a semiconductor substrate, comprising the steps of:

5 introducing a source gas comprising a compound composed of at least Si, C, and H into a chamber;
 introducing in pulses an oxidizing gas into the chamber, wherein the source gas and the oxidizing gas form a
 reaction gas; and
 forming an insulation film on a semiconductor substrate by plasma treatment of the reaction gas.

10 2. The method according to Claim 1, wherein the plasma treatment is plasma CVD processing.

3. The method according to Claim 1 or 2, wherein the compound is an organo silicon of SixCyOzHa wherein a, x, y, and z are integers.

15 4. The method according to any preceding claim, wherein the oxidizing gas is introduced in the chamber in cycles of 5msec to 10sec.

5. The method according to any preceding claim, wherein the oxidizing gas is introduced in the chamber in cycles of 100msec to 5sec.

20 6. The method according to any preceding claim, wherein the oxidizing gas is oxygen or N_2O .

7. The method according to any preceding claim, wherein the introduction of the oxidizing gas in pulses is conducted by introducing alternately (i) a first reaction gas comprising the source gas to a base flow rate and the oxidizing gas at a flow rate of 50% or higher of the base flow rate, and (ii) a second reaction gas comprising the source gas at a base flow rate and no oxidizing gas or the oxidizing gas at a flow rate of 50% or less of the base flow rate.

25 8. The method according to any preceding claim, wherein the total flow of the oxidizing gas is less than the flow of the source gas.

30 9. The method according to any preceding claim wherein the source gas further comprises an inert gas.

10. The method according to any preceding claim, wherein the pulses and the flow of the oxidizing gas is selected to adjust a dielectric constant of the insulation film to 2.45 or less.

35 11. The method according to any preceding claim, wherein a plasma is formed by RF power.

12. The method according to Claim 11, wherein the intensity of RF power is pulsed in cycles synchronized with the pulsed flow of the oxidizing gas.

40 13. The method according to Claim 11 or 12, wherein the intensity of RF power is higher in cycles when the oxidizing gas flow is low than cycles when the oxidizing gas flow is high.

45 14. The method according to any one of Claims 11 to 13 wherein the intensity of RF power is pulsed in cycles of 1msec or more.

15. The method according to any preceding claim, wherein the formation of the insulation film is conducted while maintaining a temperature of a shower plate at 150°C or higher, through which the reaction gas passes into the chamber.

50 16. The method according to any preceding claim, wherein the insulation film is a cap layer having a thickness of 10nm or more.

55

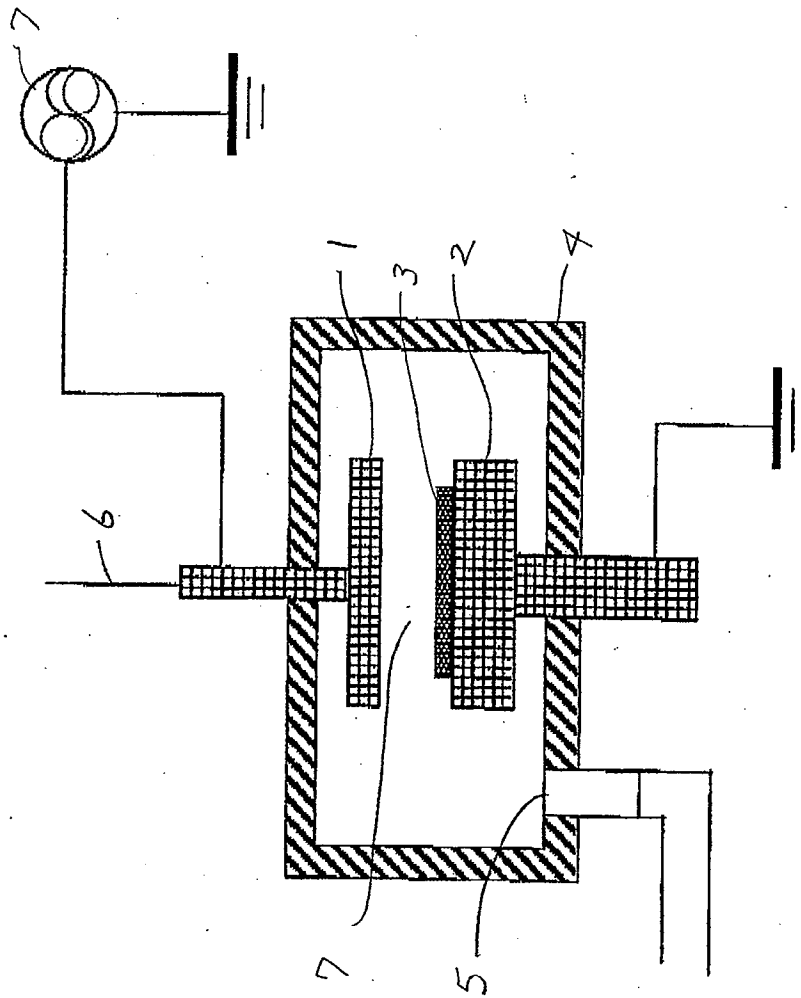


Fig.1

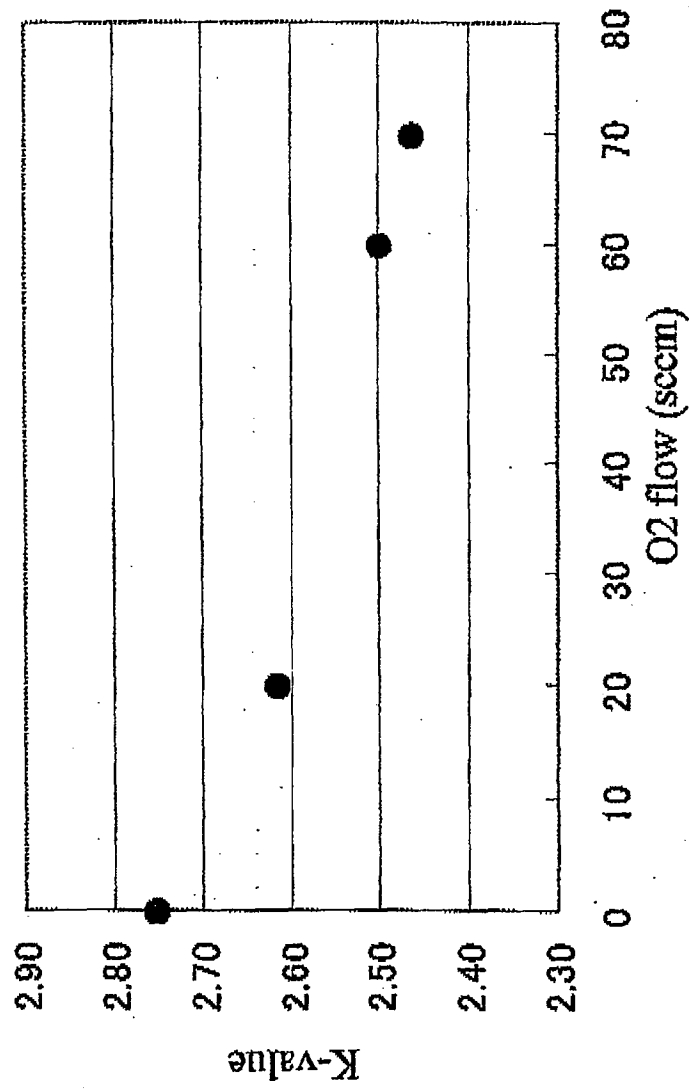


Fig. 2 : O₂ flow vs. k-value by non-pulsed process



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 0497

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 1 039 523 A (CANON SALES CO INC ; SEMICONDUCTOR PROCESS LAB CO (JP)) 27 September 2000 (2000-09-27)	1-6, 8-10,16	C23C16/455 C23C16/40
Y	* paragraphs [0083]-[0114]; figures 7,8 * ---	15	
Y	US 5 316 796 A (ARITA YOSHINOBU ET AL) 31 May 1994 (1994-05-31) * column 7, line 19 - line 64; figure 2 * ---	15	
A	NUR SELAMOGLU ET AL: "SILICON OXIDE DEPOSITION FROM TETRAETHOXYSILANE IN A RADIO FREQUENCY DOWNSTREAM REACTOR: MECHANISMS AND STEP COVERAGE" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART B, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 7, no. 6, 1 November 1989 (1989-11-01), pages 1345-1351, XP000249692 ISSN: 0734-211X * paragraph [0011] * ---	1-16	
A	US 2001/041250 A1 (HAUKKA SUVI P ET AL) 15 November 2001 (2001-11-15) * paragraphs [0060]-[0071]; figure 7 * -----	1-16	C23C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 May 2003	Examiner Ekhult, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 03 25 0497

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-05-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1039523	A	27-09-2000	JP	3236576 B2	10-12-2001
			JP	2000277515 A	06-10-2000
			EP	1039523 A2	27-09-2000
			US	6372670 B1	16-04-2002

US 5316796	A	31-05-1994	DE	4107756 A1	12-09-1991
			JP	2887240 B2	26-04-1999
			JP	4214867 A	05-08-1992
			KR	9402439 B1	24-03-1994
			US	5462014 A	31-10-1995

US 2001041250	A1	15-11-2001	US	2003032281 A1	13-02-2003
			AU	4538801 A	17-09-2001
			EP	1266054 A2	18-12-2002
			WO	0166832 A2	13-09-2001

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82